CHAPTER 1

INTRODUCTION

Between 1952 and 1970, low-level radioactive, mixed, and transuranic wastes from federal facilities were buried in unlined shallow pits, soil vaults, and trenches in surficial sediments within the Radioactive Waste Management Complex (RWMC) at the Idaho National Engineering and Environmental Laboratory (INEEL). Past disposal practices once thought to be adequate have been found to be potentially detrimental to the environment. Elevated levels of disposed radionuclides have been detected in surficial sediments, in perched waters above two principal sedimentary interbeds at 34 m and 73 m , and in the Snake River Plain Aquifer (Schmalz, 1972; Barraclough *et al.*, 1976; Knobel and Mann, 1988; Mann and Knobel, 1988; Rawson *et al.*, 1991; Bartholomay 1998). In 1989, the INEEL was added to the U.S. Environmental Protection Agency's National Priorities List and subsequent remediation efforts were begun.

In support of the remediation efforts, an interim risk assessment was initiated to determine the risk to human health and guide remediation decisions. A major portion of the remedial investigation involves modeling contaminant pathways of transport and exposure. The principal exposure route of concern is the Snake River Plain Aquifer, a major source of drinking, industrial, and irrigation water for southern Idaho. The Snake River Plain Aquifer lies approximately 180 m below the RWMC and is overlain by a sequence of volcanic rocks, primarily basalt, interbedded with several sedimentary layers deposited

during periods of volcanic quiescence (Anderson and Lewis, 1989). Groundwater from the aquifer is typically alkaline with significantly elevated bicarbonate concentrations (Wood and Low, 1986).

Modeling contaminant transport beneath the RWMC is difficult due to both the heterogeneity of the subsurface and uncertainties in hydrologic conditions and geochemical interactions affecting contaminant transport. Advection, dispersion, and geochemical interactions between the contaminant and geologic materials dominate transport in the subsurface. Hydrologic conditions control advective/dispersive mechanisms and are beyond the scope of this research. This research focused on the quantification of geochemical interactions between the selected contaminants and geologic materials in the subsurface.

Clemson University has undertaken both batch and column laboratory tests to examine geochemical interactions and determine transport parameters in the subsurface for long-lived radionuclides in support of the risk assessment (Goff, 1994; Fjeld et al., 2000). Application of the results from these investigations to the risk assessment has been approached with caution. The results represent unique points from experimental environments that may not have replicated actual field conditions on two accounts: (1) previous experimental protocol required the combination of five separate interbed samples into a single homogenized sample consisting of the fine fraction (Dia. < 250 nm); (2) groundwater simulants used in the early investigations contained lower concentrations of most constituents than the average groundwater reported by Wood and Low (1986).

First, the homogenization of sedimentary interbed material in previous experiments probably resulted in samples with significantly different grain size distributions and mineralogy from those of the original sediments leading to unique sorption characteristics (USGS, 1999). Additionally, use of the fine fraction eliminated 40 percent of the solids and may have biased distribution coefficients toward higher values due to the fraction's greater surface area (USGS, 1999).

Secondly, the low ionic strength of the experimental simulants used in previous studies probably resulted in less competition for surface sites thereby increasing the observed sorption. Furthermore, the simulants were undersaturated with respect to calcite, a common carbonate mineral phase in the sedimentary interbeds, possibly resulting in increased sorption due to the absence of mobile carbonate complexes.

The primary goal of this research was to characterize sorption of a select suite of radionuclides under conditions that are more representative of actual field conditions beneath the RWMC than in previous studies. The contaminants of concern were uranium, neptunium, americium, and chromium. Uranium, neptunium, and americium are common components of transuranic defense wastes while chromium is an anti-corrosion agent. The research focused specifically on the characterization of the sorption isotherms, the variability of sorption among distinct soil samples, and the effect of selected groundwater constituents on sorption behavior.

To improve the spatial resolution of sorption behavior, 14 depth-discrete interbed grab samples from beneath the RWMC were used as the solid phase for batch studies. The actual groundwater composition beneath the RWMC is subject to variability due either to natural heterogeneity or to perturbations from buried wastes. Bicarbonate is probably the most important groundwater constituent at the INEEL due to its ubiquity and contribution to contaminant mobility. Additionally, there is experimental evidence suggesting sulfate and fluoride may affect contaminant mobility (Fjeld *et al.*, 2000). Complexation of the contaminants of concern with carbonate, sulfate, and fluoride may significantly alter their transport behavior due to the influence of these species on aqueous speciation. Thus the effects of complexation with bicarbonate, sulfate, and fluoride ligands upon sorption behavior were of interest.

CHAPTER 2

OBJECTIVES

The goal of this investigation was to characterize sorption of ^{51}Cr, ^{233}U, ^{237}Np, and ^{241}Am in interbed grab samples from the RWMC at the INEEL. The specific objectives of this research were:

1. To characterize the sorption isotherms from batch sorption studies for ^{51}Cr, ^{233}U, ^{237}Np, and ^{241}Am equilibrated in synthetic groundwater representative of typical INEEL groundwater as characterized by Wood and Low (1986) in contact with 14 interbed grab samples from the RWMC.

2. To determine the variability of sorption among 14 interbed grab samples collected at distinct depths from the RWMC.

3. To determine the effect of bicarbonate, sulfate, and fluoride on sorption behavior.

CHAPTER 3

ENVIRONMENTAL GEOCHEMISTRY

Geochemical interactions in subsurface environments may significantly influence contaminant mobility. An assortment of solid and liquid phase processes can contribute to geochemical interactions including oxidation-reduction, complexation, precipitation, and sorption. This chapter reviews current scientific understanding of the geochemical interactions believed to exert significant influence on contaminants' mobility at the RWMC.

Aqueous Contaminant Speciation

The contaminants of concern for this research are all heavy metals resulting from the filling of underlying electron orbitals: 3-d for chromium and 5-f for the actinides americium, neptunium, and uranium. The variety of electronic structures associated with these underlying electron orbitals permits a variety of oxidation states for elements of these series. Consequently, these elements have a propensity to form multiple complexes, which may alter mobilities. The contaminants are all hard acids in the oxidation states expected for typical INEEL groundwater and preferentially form electrostatic bonds with highly electronegative ligands such as oxygen donors. Their affinity to form complexes is relative to their respective effective charges (Stumm and Morgan, 1996). Therefore, the relative affinity for the actinides to form complexes generally follows the sequence: (Hobart, 1990)

$$An(IV) > An(III) \approx An(VI)O_2^{2+} > An(V)O_2^+,$$
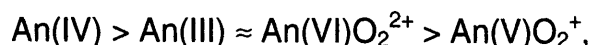
where An represents an actinide element. Additionally, the strengths of various groundwater ligands are crucial to complex formation. The relative strengths for common inorganic groundwater ligands are typically: (Langmuir, 1997)

$$OH^- > CO_3^{2-} > F^- > HPO_3^{2-} >> Cl^-, NO_3^-$$
$$and$$
$$PO_4^{3-} >> HPO_4^{2-} > SO_4^{2-}$$
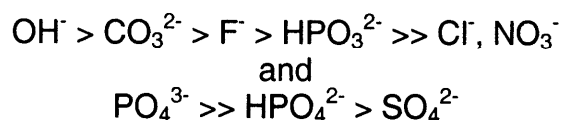
Chromium

Chromium exhibits a variety of oxidation states, -II to +VI. In the natural environment, chromium typically exists in either the trivalent or the hexavalent oxidation state. Trivalent chromium exhibits the largest range of stability and is believed to be the predominant state at the INEEL. Oxidation of the trivalent to the hexavalent state has only been experimentally shown to occur in the presence of higher valence manganese oxides (Schroeder and Lee, 1975; Bartlett and James, 1979; Eary and Rai, 1987).

The significant aqueous trivalent chromium species below pH 3.5 is the hydrated cation (Baes and Mesmer, 1976). As pH increases, hydrolyzed species begin to dominate. Major solution species and their pH range of dominance include: $CrOH^{2+}$ from pH 3.8 to 6.4, $Cr(OH)_3^{o}(aq)$ from pH 6.4 to 10.5, and $Cr(OH)_4^-$ above pH 11.5 (Rai et al., 1987). At environmental concentrations, reported polynuclear species are not expected to be significant (Rai et al., 1987).

The solubility of trivalent chromium is limited by the formation of $Cr(OH)_3(s)$. $Cr(OH)_3(s)$ is expected to maintain dissolved chromium levels below 10^{-5} M between pH 6 and 12 (Rai et al., 1987). Additionally, in the presence of

dissolved iron, trivalent chromium co-precipitates with ferric iron to form the solid solution [Fe,Cr](OH)$_3$ which has a lower energy of formation and faster kinetics than Cr(OH)$_3$(s) (Sass and Rai, 1987).

Uranium

Uranium exists in a variety of oxidation states, +III to +VI. Under normal environmental conditions, uranium can potentially exist in three oxidation states: tetravalent, pentavalent, and hexavalent. However, the pentavalent state is unstable due to disproportionation, and only the tetravalent and hexavalent states are of long-term consequence (Hobart, 1990). Tetravalent uranium is more stable in reducing environments while the hexavalent state becomes predominant an more oxidative environments. The hexavalent state is expected to be the predominant uranium oxidation state under Eh-pH conditions typical of the INEEL (Brookins, 1988).

In pure water, hydrolysis begins to become important near pH 5. In the pH range 5 to 9, $UO_2(OH)_2^o$(aq) is expected to be the dominant hexavalent species, while $UO_2(OH)_3^-$ becomes more significant between pH 9 and 10 (Grenthe et al., 1992). Polynuclear complexes can become significant at higher total uranium(VI) concentrations (Morris et al., 1994).

In more chemically complex waters, several uranyl species are likely to exist. Under acidic conditions and significant fluoride concentrations, UO_2F^+ is expected to dominate (Patil and Ramakrishna, 1976). Above pH 5, hexavalent uranium predominately forms carbonate complexes dependent upon total carbonate concentrations. Major solution species for typical natural waters

include $UO_2CO_3^0$(aq), $UO_2(CO_3)_2^{2-}$, and $UO_2(CO_3)_3^{4-}$ (Scanlan, 1977; Ciavatta, et al., 1979; Maya, 1982; Grenthe et al., 1984; Grenthe and Lagerman, 1991). At lower total carbonate levels, $(UO_2)_2CO_3(OH)_3^-$ can be significant depending on dissolved uranium concentrations (Grenthe and Lagerman, 1991). Fluoride and sulfate complexes may become significant when their respective concentrations are high. However, their stabilities are considerably less than the carbonate complexes (Grenthe et al., 1992).

Hexavalent uranium is generally very soluble due to the formation of the carbonate complexes. A potentially major solid uranyl species in the absence of sufficient carbonate is schoepite, UO_3-$2H_2O$(c), which may limit total uranium below 10^{-5} M between pH 5 and 9 (Grenthe et al., 1992).

Neptunium

Neptunium exhibits a variety of positive valences ranging from trivalent to heptavalent. In natural waters, neptunium potentially exists in three distinct oxidation states: tetravalent, pentavalent, and hexavalent. Due to the instability of the hexavalent state in all but the most oxidizing solutions, only the tetravalent and pentavalent states are of long-term consequence (Hobart, 1990). The tetravalent state is stable over a wide range of environmental conditions. However, the Eh-pH conditions at the INEEL suggest that the pentavalent state is also likely to form (Brookins, 1988). Additionally, the pentavalent state should be the dominant aqueous oxidation state since the tetravalent state is generally insoluble.

Due to its lower effective charge, neptunyl, NpO_2^+, is very stable particularly towards hydrolysis. In carbonate-free waters where hydroxide is the only complexing ion, hydrolysis does not become significant until near the pH range 10 to 11. Below pH 10, the neptunyl ion dominates pentavalent neptunium speciation. Above pH 11, major solution species include $NpO_2OH^o(aq)$ and $NpO_2(OH)_2^-$ (Lierse et $al.$, 1985; Itagaki et $al.$, 1992; Neck et $al.$, 1992).

In complex aqueous environments, NpO_2^+ again exhibits a wide range of stability, predominating up to pH 7.5. Above pH 9, carbonato complexes begin to dominate speciation. Major solution species are expected to be $NpO_2CO_3^-$ and $NpO_2(CO_3)_2^{3-}$ (Maya, 1983; Bidoglio et $al.$, 1985; Inoue and Tochiyama, 1985; Grenthe et $al.$, 1986; Nitsche et $al.$, 1990; Neck et $al.$, 1994). The triscarbonato complex is considered negligible in dilute solutions (Neck et $al.$, 1994). Mixed hydroxide-carbonate complexes may become significant only above pH 11 (Neck et $al.$, 1997). Experimentally, little is known about the fluoride or sulfate complexes. However, these complexes are probably considerably less significant than the carbonate and hydroxide species due to their relative affinity to complex and the wide stability of NpO_2^+.

Neptunium(V) is generally quite soluble in natural waters due to the stability of the neptunyl ion. Aqueous neptunium is generally limited by the formation of $NpO_2OH(s)$, which may keep concentrations below 10^{-6} M between pH 11 and 12 (Lierse et $al.$, 1985; Neck et $al.$, 1992; Neck et $al.$, 1995a; Runde et $al.$, 1996). Solubility decreases with time and increasing ionic strength due to aging of the amorphous $NpO_2OH(s)$ (Neck et $al.$, 1992; Neck et $al.$, 1995a;

Runde *et al.*, 1996). In the pH range less than 11, solubility increases generally due to the predominance of NpO_2^+ and carbonato complexes over hydrolyzed species.

In carbonate-bearing solutions, sodium neptunyl carbonates are expected to control solubility at $[Na+] \geq 10^{-1}$ M. $NaNpO_2CO_3(s)$ is the stable species below pH 8.5, however, will slowly convert to the less soluble $Na_3NpO_2(CO_3)_2(s)$ above pH 9 depending on carbonate concentration (Neck *et al.*, 1994; Neck *et al.*, 1995a,b; Runde *et al.*, 1996).

Americium

Americium can exhibit a variety of positive oxidation states from divalent to heptavalent. However, due to large reduction-oxidation potentials, the trivalent form is the only oxidation state expected under normal environmental conditions (Hobart, 1990). Under acidic conditions, the hydrated cation dominates speciation. Above a pH range of 5.5 to 7.5, trivalent americium predominately forms carbonate complexes dependent upon total carbonate concentrations. Major solution species include $AmCO_3^+$, $Am(CO_3)_2^-$, and $Am(CO_3)_3^{2-}$ (Bidoglio, 1982; Lundqvist, 1982; Nitsche *et al.*, 1989; Felmy *et al.*, 1990; Meinrath and Kim, 1991). The existence of bicarbonate and mixed hydroxide-carbonate complexes, though suggested, is disputed due to experimental shortcomings (Silva *et al.*, 1995). At low carbonate concentrations, hydrolyzed species may become more influential. The solution phase concentration of americium is limited by the formation of $AmOHCO_3(c)$, which will likely maintain dissolved

americium below 10^{-8} M between pH 7 and 9 (Silva and Nitsche, 1984; Runde *et al.*, 1992; Vitorge, 1992).

Sorption

A contaminant's affinity to the solid phase may be significant in regulating its transport behavior. Contaminants typically become associated with the soil matrix through adsorption, a two-dimensional accumulation at the solid-liquid interface; absorption, a three-dimensional transfer into the soil matrix; or surface precipitation, in which a three-dimensional moiety forms at the interface in the absence of the same species in solution. When the exact process is unclear, the term sorption is commonly used to refer to the association of contaminants with solid phases.

Interfacial Forces

Sorption occurs when an affinity exists between a sorbate, the solute undergoing sorption, and the sorbent, the phase where association occurs. An affinity to the solid-liquid interface arises from a net attractive force at the interface. These forces are often explained according to forces governing intermolecular interactions and are commonly categorized as physical or chemical depending on which interactions exert a significant effect on the sorption process, though all forces can act simultaneously.

Physical forces are often associated with interactions between unbound discrete atoms and molecules. Physical forces include pure electrostatic interactions, as in ion-ion and ion-dipole interactions, and induced polarization interactions due to the presence of an adjacent electric field, involve both

relatively strong and weak energies of association, and can extend over comparatively large intermolecular distances (Isrealachvili, 1992).

Chemical forces generally result from the formation of chemical bonds between the sorbate and sorbent surface groups, involve large energies of attraction, but require very short distances so that electron clouds can overlap (Isrealachvili, 1992).

Surface Complex Formation

Competing interactions originating from bulk phases distort the arrangements of molecules at the solid-liquid interface from those in the respective bulk phases leading to the development of surface charge (Sposito, 1984). Specifically, surface charge results from either ionizable groups that associate with the solid phase at the solid-liquid interface or lattice imperfections caused by isomorphic substitutions (Stumm and Morgan, 1996). When surfaces acquire charge different from their surroundings, counter-charges accumulate adjacent to the surface to maintain electroneutrality leading to the formation of the electric double layer. The electric double layer consists of charged surface sites and the accumulation of both compact and diffuse liquid phase counter ions adjacent to the solid surface (Grahame, 1947). The accumulation of counter ions at the solid-liquid interface is hypothesized to occur through reactions analogous to those that occur in solution, i.e., complex formation (Davis et al., 1978).

On clays and oxide surfaces, the most reactive components of inorganic soils, the hydroxyl group is the most significant surface functional group (Sposito,

1984). The adsorption of metals or ligands on surface hydroxyls is envisaged as competitive complex formation; for example (Stumm and Morgan, 1996)

$$\equiv S\!-\!OH + M^+ \ \Box \equiv S\!-\!OM + H^+$$
or
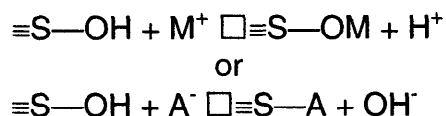$$\equiv S\!-\!OH + A^- \ \Box \equiv S\!-\!A + OH^-$$

Figure 3.1 depicts the three mechanisms of surface adsorption for ions at oxide surfaces. Ions approaching a solid-liquid interface may form strongly bound inner-sphere complexes, outer-sphere complexes in which one or more solvation shells separate the ion from the base, or remain in the diffuse ion swarm near the interface (Hayes and Leckie, 1987).
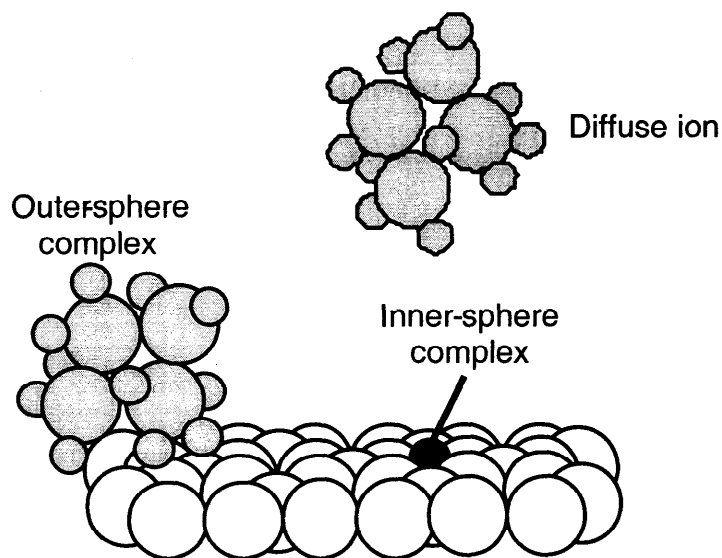

Figure 3.1   Adsorption mechanisms at oxide surfaces.
(Adapted from Sposito, 1989). Inner-sphere complexes may retain their solvation shells away from the solid surface.

Sorption Models

Several empirical models exist which characterize the equilibrium distribution of a contaminant among the solution and sorbent phases. Typically,

these models relate the amount of contaminant sorbed per unit mass of sorbent, S, to the amount of contaminant remaining in solution, C, at a fixed temperature and pressure, and are referred to as isotherms. Three widely used classical sorption models are the Linear, Langmuir, and Freundlich isotherms.

Linear

The simplest model describing sorption phenomena is the linear model or distribution ratio. In the linear model, the amount of sorbate accumulated on the sorbent surface is directly proportional to the solution phase concentration:

$$S = K_D C \tag{1}$$

The proportionality constant, K_D, is commonly termed the distribution coefficient. This model is appropriate when the sorbate's affinity for the sorbent remains uniform across varying concentrations. The linear model is a good approximation for low solute concentrations and for soils with low sorption potential (Weber et al., 1991).

Langmuir

Although Langmuir's (1918) sorption isotherm was originally developed for gases on solid surfaces, it has also been widely applied to aqueous species on soils. The model describes sorption in which the sorbate accumulates on a finite quantity of localized sorption sites in a single layer. Since sorption sites are limited, the relationship between aqueous and solid phase concentrations is nonlinear. According to the Langmuir model the energy of association for each

contaminant molecule is constant, and there are no interactions between sorbate

molecules (Langmuir, 1918). The expression, derived from mass law, is

$$S = S_{max} \frac{K_L C}{1 + K_L C}$$

(2)

where S_{max} represents the finite capacity of sites on the sorbent available to the

contaminant, and K_L is a measure of bond strength holding the sorbate to the

sorbent.

Freundlich

The Freundlich isotherm was the first sorption isotherm developed. It also

describes the accumulation of a solute onto sorption sites as a nonlinear

equilibrium process. It is actually a special case of the Langmuir equation in

which the energy of association is a logarithmic distribution of surface coverage

(Sposito, 1980). The Freundlich model takes the form

$$S = K_F C^n$$

(3)

where K_F relates to sorption capacity and n is a measure of non-linearity. The

Freundlich isotherm models sorption onto solids with heterogeneous surfaces

well but does not provide for a maximum of adsorption. This model may be the

most widely used classical sorption isotherm (Weber et al., 1991). However, the

flexibility of two adjustable parameters does not guarantee extrapolation of the

Freundlich beyond the experimental data set (Travis and Eitner, 1981).

CHAPTER 4

MATERIALS AND METHODOLOGY

Materials

Groundwater Simulant

The aqueous phase used for all batch experiments was a synthetic groundwater solution based on Wood and Low's (1986) characterization of the Snake River Plain Aquifer and should be typical of the groundwater beneath the RWMC. Groundwater from the Snake River Plain Aquifer is typically alkaline with significant bicarbonate concentration. Data summarizing Wood and Low's (1986) characterization of major cations and anions in the Snake River Plain Aquifer are listed in Table 4.1. Three distinct chemical compositions of groundwater simulants were used for the batch partitioning studies. Acronyms used to differentiate formulations of groundwater simulants used in this investigation are also listed in Table 4.1, which includes the chemical composition of each. Simulants noted in Table 4.1 include a groundwater simulant (GWS), which was formulated for the major cations and anions found in the Snake River Plain Aquifer, and GWS in which specific chemical constituents were removed. For example, GWS($-CO_3^{2-}$) denotes the base groundwater simulant minus the carbonate ion. Each simulant was prepared using reagent grade chemicals and deionized distilled water. Dilute hydrochloric acid and sodium hydroxide were used to adjust pH.

Table 4.1 Composition of Snake River Plain Aquifer (SRPA) groundwater and the groundwater simulants used in this study.

| COMPONENT | SRPA GROUNDWATER[†] | | | GROUNDWATER SIMULANTS | | |
| | Mean | Maximum | Minimum | GWS | GWS $(-CO_3^{2-})$ | GWS $(-CO_3^{2-}, SO_4^{2-}, F^-)$ |
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Ca^{2+}	51	120	5	51	51	51
K^{1+}	4	12	0	4	N/A	N/A
Mg^{2+}	18	54	0.2	18	18	7.7
Na^{1+}	26	140	3.9	181	101	100
Cl^{1-}	28	230	1.8	112	113	113
SO_4^{2-}	41	218	2.7	41	41	N/A
HCO_3^{1-}	220	510	52	220	Trace	Trace
F^{1-}	0.6	11	0.6	0.6	0.7	N/A
SiO_2	50	138	5.8	50	50	50
pH	7.8	9.1	7.0	8.0±0.2	8.0±0.2	8.0±0.2
I	0.008	0.02	0.002	0.014	0.010	0.009

[†]Data based on Wood and Low's (1986) characterization of the Eastern Snake River Plain Aquifer.

Sedimentary Interbed

The solid phase in all batch experiments consisted of 14 depth-discrete grab samples from the OU 7-13/14 well installation at the RWMC. Tables 4.2, 4.3, and 4.4 list the collection depths and soil characterization data, when available, for the 14 grab samples. The grab samples were air-dry sieved using U.S. Standard Testing sieves meeting ASTM E-11 specifications and the fraction less than 2 mm was retained. A more detailed description of the particle size distributions of the grab samples is presented when available in Appendix A. The Southwest Research Institute performed the soil characterizations under INEEL statement of work number ER-SOW-371. The retained fractions (< 2 mm) of the 14 soil samples used for this investigation were pretreated with the appropriate groundwater simulant at a solids concentration of approximately 300,000 mg/L.

The pretreatment process involved four contact intervals: three 15 min. and one 24 hr. Each contact interval involved orbital shaking at 300 RPM for the specified time followed by centrifugation at 1000X g for 5 min. and decanting of the contact solution. Centrifugation at these speeds was not sufficient to settle colloidal material, which would have remained suspended in the contact solution. Therefore, the colloids would have been lost after decanting. Colloids have high surface area to volume ratios relative to larger diameter particles. Therefore, the sorption affinity of colloids should be greater than for larger particles. The loss of colloids during pretreatment would have likely biased distribution coefficients toward lower values.

Following pretreatment, soil suspensions were produced for the partitioning studies with the pretreated soil in the appropriate groundwater simulant. Typical solids concentrations ranged from 50,000 to 100,000 mg/L. The actual solids concentration for each experiment is listed in Appendix B.

Radionuclide Preparations

The mobility of chromium, americium, neptunium, and uranium through the sedimentary interbed beneath the RWMC was of primary concern for this investigation. Therefore, batch-spiking solutions were prepared at high activity and low volume for each of the radionuclides in the appropriate groundwater simulant and added to contact tubes in small volume to minimize the additional

Table 4.2   Summary of bulk characteristics for INEEL soils where available.

| SOIL | BULK PROPERTIES[†] | | |
| | Depth | Surface Area | CEC |
	ft	m²/g	meq/100g
7DS00101KD	103.0-103.6	75.2	43.9
7DS00301KD	107.4-108.0	61.4	23.2
7DS00501KD	238.1-238.6	46.4	19.4
7DS00701KD	103.0-103.5	19.3	14.8
7DS00901KD	112.0-112.5	51.1	27.3
7DS01701KD	231.0-231.5	36.6	23.2
7DS02301KD	230.0-230.5	34.0	22.5
I2S-INEEL-105	104.5-105.0	N/A	N/A
I1S-INEEL-109	109.0-109.4	N/A	N/A
I4D-INEEL-224	224.2-224.8	N/A	N/A
I3D-INEEL-229	229	N/A	N/A
I4D-INNEL-231	230.5-231.0	N/A	N/A
I1D-INNEL-234	234.0-234.5	N/A	N/A
I4D-INNEL-234	233.5-234.0	N/A	N/A

[†]Work performed by the SwRI under INEEL ER-SOW-371.

Table 4.3   Summary of clay fraction characteristics for INEEL soils where available.

SOIL	CLAYS[†]			
	Total Fraction %	Smectite Fraction % of Clay	Illite Fraction % of Clay	Kaolinite Fraction % of Clay
7DS00101KD	2.2	75	4	21
7DS00301KD	20.8	61	15	25
7DS00501KD	6.6	32	65	4
7DS00701KD	5.5	71	9	20
7DS00901KD	55.8	66	11	22
7DS01701KD	N/A	44	29	27
7DS02301KD	53.0	49	22	29

[†]Work performed by the SwRI under INEEL ER-SOW-371.

Table 4.4   Summary of mineral oxide characteristics for INEEL soils where available.

SOIL	EXTRACTABLE METALS[†]			
	SiO_2 % as Oxide	Al_2O_3 % as Oxide	Fe_2O_3 % as Oxide	MnO % as Oxide
7DS00101KD	0.28	0.093	1.7	0.066
7DS00301KD	0.22	0.11	1.0	0.057
7DS00501KD	0.15	0.092	0.56	0.035
7DS00701KD	0.12	0.049	0.59	0.014
7DS00901KD	0.17	0.082	0.85	0.041
7DS01701KD	0.19	0.073	1.5	0.026
7DS02301KD	0.26	0.083	1.3	0.027

[†]Work performed by the SwRI under INEEL ER-SOW-371.

volume and ionic strength effects on the partitioning studies. Spiking solutions were typically prepared via the addition of a known activity of an acid radionuclide stock to the appropriate groundwater simulant followed by a pH adjustment to 8.0±0.2 using dilute hydrochloric acid or sodium hydroxide.

Typically, five target batch radionuclide concentrations were obtained via dilution of the concentrated spiking solution in the contact vessel and varied over a range of 10 to 200 Bq-mL^{-1}. The actual initial aqueous phase concentrations of each radionuclide for each experiment are listed in Appendix B. The uranium isotopes of concern were uranium-235 and uranium-238. However, uranium-233 was used in these experiments because of its higher specific activity. Activity and molar concentration equivalents for natural uranium (99.3% U-238; 0.7% U-235) are presented in Appendix B. Although uranium-233 has a higher activity concentration, its associated mass concentration is lower than a natural uranium mass concentration due to uranium-233's higher specific activity.

Methodology

Batch Kinetic Studies

The approach to equilibrium for each radionuclide was monitored at the middle radionuclide concentration by selecting two of the 14 soil samples and equilibrating in GWS over a period of two months. Triplicate samples were sacrificed at four intervals during the two-month period to measure the aqueous phase concentration.

Kinetic studies were performed in 15 mL polypropylene contact tubes (Falcon Blue Max, Jr., Becton Dickinson Labware), which were tumbled at approximately 25 RPM. Contact tubes were centrifuged at 1000X g for 30 min to separate the solids from contact solution. Samples of 1.5 mL contact solution were filtered through a modified polyethersulfone membrane centrifugal concentrator (MicroSep 30K, Pall Filtron) for 30 min. at 5000X g to remove

colloids less than nominal 12 nm diameter. The aqueous phase concentration was measured via liquid scintillation counting (Wallac 1415, Wallac, Inc.) in a 1:10 ratio of filtered aqueous phase to scintillation cocktail (OptiPhase 'HighSafe' 2, Wallac, Inc.).

The approach to equilibrium was monitored by the change in observed distribution ratios over time. Observed distribution ratios, K's, were calculated from experimentally determined aqueous phase concentrations, C_t, at sampling time, t, and solids concentrations, SS, according to

$$K = \frac{C_{o,t} - C_t}{C_t} \bullet \frac{1}{SS} \qquad (4)$$

where $C_{o,t}$ represents the initial aqueous phase concentration decay corrected to sampling time, t (Goff, 1994). When changes in observed distribution coefficients were small, the system was considered to be a sufficient approximation of equilibrium conditions.

Batch Equilibrium Studies

Equilibrium partitioning studies were based on the ASTM D-4319-93 specifications to determine observed distribution ratios for chromium, americium, neptunium, and uranium on the 14 sedimentary interbed samples (ASTM, 1993). Partitioning study samples were incubated for a time period sufficient to approximate equilibrium conditions as determined by the kinetic studies. Aqueous phase concentrations were determined according to the same procedure used to process samples for the kinetic studies. Sorbed phase

concentrations, S, were calculated from the aqueous phase concentrations, C_t, at sampling time, t, and solids concentrations, SS according to

$$S = (C_{o,t} - C_t) \bullet \frac{1}{SS} \tag{5}$$

where $C_{o,t}$ represents the initial aqueous phase concentration decay corrected to sampling time, t (Goff, 1994). Background (no activity) and blank samples (no soil) were analyzed to determine the activity present in the soil prior to the study and the loss of activity in the absence of soil respectively. All samples were prepared in duplicate.

Inorganic Carbon Analysis

Determination of the apparent equilibrium inorganic carbon concentration was determined with a total organic carbon analyzer (TOC-5050, Shimadzu Corp.) in quadruplicate background samples (no activity) for each groundwater simulant. Equilibrated samples were centrifuged and filtered as for the partitioning studies. Three inorganic carbon standards, which varied from 15 to 300 mg/L, were prepared in triplicate from oven-dry (285 °C) reagent grade sodium bicarbonate and sodium carbonate in deionized distilled water, which was equilibrated with the atmosphere, to quantify analyzer response. The response curve is plotted in Appendix B.